Supporting Information

Synthesis, aggregation induced emission and through space conjugation of triphenylvinylphenyl substituted [2.2]paracyclophane-1,9-diene

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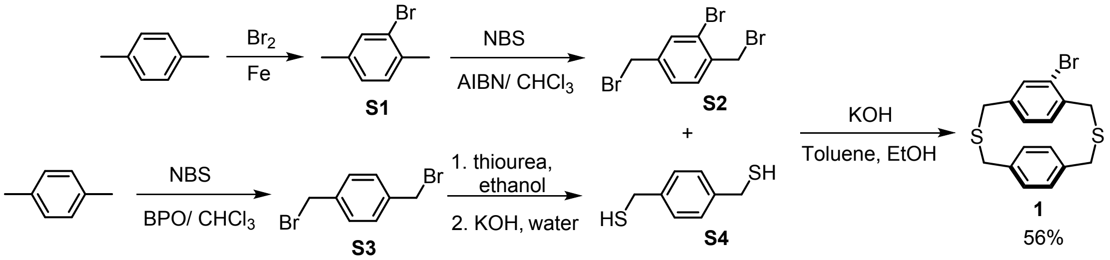


Scheme S1. Synthetic route to compound **1**.

Synthesis

Synthesis of 2-bromo-1,4-dimethylbenzene **S1**

Bromine (8.2 mL, 0.16 mol) was added dropwise to a suspension of *p*-xylene (19.8 mL, 0.16 mol) and iron (0.16 g, 2.86 mmol) at 15°C and was stirred for 16 hours at room temperature. The reaction was quenched with sodium bisulfite solution and extracted with DCM and water. The organic layers were combined, dried with $MgSO_4$ and evaporated to give a clear oil. The resulting oil was then purified by fractional distillation under reduced pressure at 85°C to give transparent oils in 65% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (s, 1H, Ar*H*), 7.10 (d, J = 7.8 Hz, 1H, Ar*H*), 7.00 (d, J = 7.8 Hz, 1H, Ar*H*), 2.35 (s, 3H, -C*H*$_3$), 2.29 (s, 3H, -C*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.34, 134.71, 132.09, 130.63, 120.14, 124.78, 22.49, 20.67. Mass spectrum (EI, M$^+$): 184 *m/z*.

Synthesis of 2-bromo-1,4-bis(bromomethyl)benzene **S2**

2-bromo-1,4-dimethylbenzene **S1** (40.74 g, 0.22 mol), *N*-bromosuccinimide (79.14 g, 0.44 mol) and azobisisobutyronitrile (0.271 g, 1.65 mmol) was added into chloroform

(250 mL) and refluxed for 4 hours. After cooling to room temperature, the resulting solution was extracted with DCM and sodium bisulfite solution, dried with $MgSO_4$ and removed the solvent under reduced pressure. The residue was recrystallized in ether and obtained as the white solids with 40% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (d, J = 1.8 Hz, 1H, Ar*H*), 7.43 (d, J = 7.8 Hz, 1H, Ar*H*), 7.32 (dd, J = 7.8, 1.8 Hz, 1H, Ar*H*), 4.58 (s, 2H, $-CH_2Br$), 4.41 (s, 2H, $-CH_2Br$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.09, 137.28, 133.84, 131.64, 128.70, 124.62, 32.8, 31.43. Mass spectrum (EI, M^+): 340 *m/z*. M.P.: 92°C.

Synthesis of 1,4-bis(bromomethyl)benzene **S3**

p-Xylene (8.5 g, 80 mmol), *N*-bromosuccinimide (29.9 g, 168 mmol) and benzoyl peroxide (0.5 g, 2 mmol) was added into chloroform (250 mL) and refluxed for 5 hours. After cooling to room temperature, the resulting solution was extracted with DCM and sodium bisulfite solution, dried with $MgSO_4$ and removed the solvent under reduced pressure. The crude compound was purified by recrystallization with ether to give the 52% yield.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (s, 4H), 4.48 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.97, 129.44, 32.77. Mass spectrum (EI, M^+): 262 *m/z*. M.P.: 145°C.

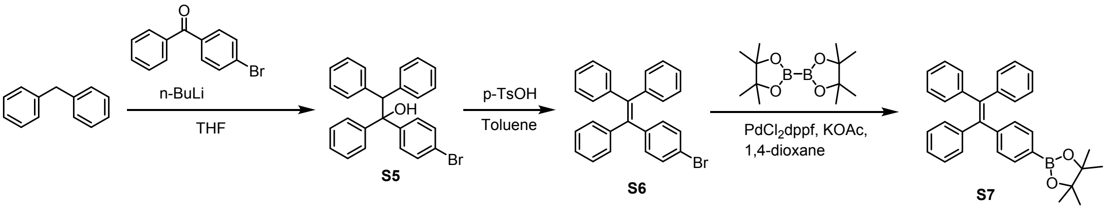
Synthesis of 1,4-phenylenedimethanethiol **S4**

1,4-Bis(bromomethyl)benzene **S3** (11.6 g, 44 mmol) and thiourea (8.04 g, 105.6 mmol) were dissolved in ethanol (160 mL) and stirred under reflux for 5 hours. The reaction was cooled and then removed most of the solvent. The remaining white solid was heated under reflux with deoxygenated solution of KOH (10.89 g, 194 mmol) in water (300 mL) for another 5 hours. The aqueous H_2SO_4 was slowly added into the cooled alkaline solution. The resulting dithiol was extracted with ether and brine, dried with $MgSO_4$ and evaporated to give a yellow oil. The crude compound was purified by column chromatography using a solvent system of DCM: hexane (1:4) and the pure product was obtained as a pale solid in a yield of 91%.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (s, 4H), 3.73 (d, J = 7.8 Hz, 4H), 1.75 (t, J = 7.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.10, 128.49, 28.74. Mass spectrum (EI, M^+): 170 *m/z*. M.P.: 47°C.

Synthesis of 5-bromo-2,11-dithia[3.3]paracyclophane **1**

A deoxygenated toluene solution (500 mL) of **S2** (10.29 g, 30 mmol) and **S4** (5.11 g, 30 mmol) was added dropwise to a solution of KOH (4.2 g, 75 mmol) in ethanol (1000 mL) under an argon atmosphere for a period of 72 hours at room temperature. After stirring for another 6 hours, the solvent was evaporated and the residue was extracted with DCM and aqueous HCl several times. The organic layers were combined, dried with anhydrous $MgSO_4$ and evaporated. The resulting white solid was then purified by column chromatography (DCM: hexane, 1:4 (v/v)) to give white solids in a yield of 56%. ^1H NMR (600 MHz, $CDCl_3$, δ): 7.07 (s, 1H, ArH), 7.05 (d, 1H, ArH), 7.03 (d, J = 7.8Hz, 1H, ArH) , 6.99 (dd, J =7.8, 1.8 Hz, 1H, ArH) , 6.97 (d, J = 7.8Hz, 1H, ArH) , 6.83 (d, J = 8.4 Hz, 1H, ArH) , 6.81 (d, J = 8.4 Hz, 1H, ArH), 4.23 (d, J = 15.0 Hz, 1H, $ArCH_2S$-), 3.87 (d, J = 15.0 Hz, 1H, $ArCH_2S$-), 3.80 (s, 2H, $ArCH_2S$-), 3.78 (d, J = 15.0 Hz, 1H, $ArCH_2S$-), 3.75 (s, 2H, $ArCH_2S$-), 3.66 (d, J = 15.0 Hz, 1H, $ArCH_2S$-). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 137.95, 135.77, 135.68, 134.47, 133.25, 132.12, 129.91, 129.62, 129.51, 129.06, 127.91, 124.01, 38.54, 37.87, 37.67, 37.38. HRMS (EI, M^+): calculated for $[C_{16}H_{15}BrS_2]^+$: *m/z* 349.9799, found *m/z* 349.9797. M.P.: 198°C.



Scheme S2. Synthetic route to 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane **S7**.

Synthesis of 1-(4-bromophenyl)-1,2,2-triphenylethylene **S6**

Diphenylmethane (4.04 g, 24 mmol) was dissolved in anhydrous THF (50 mL) under an argon atmosphere and the reaction solution was cooled to 0°C. After adding n-butyllithium (2.5 M in hexane, 8.0 mL, 20 mmol) slowly, a solution of 4-bromobenzophenone (4.7 g, 18 mol) in anhydrous THF (25 mL) was added dropwise with dropping funnel. The solution was allowed to warm up to room temperature and kept stirring for another 8 hours. The reaction mixture was quenched by saturated aqueous NH_4Cl and solvent was removed by rotary evaporator. The residue was extracted with DCM and water, dried with $MgSO_4$, and removed the solvent to obtain **S5** without further purification (4.77 g, 61 %). Compound **S5** (4.00 g) and p-TsOH(0.4 g, 2.3 mmol) were dissolved in 100 mL of toluene and the reaction mixture was reflux with Dean-Stark trap apparatus for overnight. The reaction mixture was cooled to room temperature and washed with brine and dried over $MgSO_4$. The solvent was removed by rotary evaporator and the residue was purified by flash column chromatography using hexane as an eluent to give a white solid (3.04 g) in a yield of 82 %.

^1H NMR (600 MHz, $CDCl_3$): δ 7.22 (d (AA'BB'), 2H, J = 8.5 Hz), 7.15-7.07 (m, 9H), 7.05-6.99 (m, 6H), 6.90 (d (AA'BB'), 2H, J = 8.5 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.45, 143.36, 143.26, 142.74, 141.65,139.70, 133.02, 131.33, 131.28, 131.26, 130.89, 127.92, 127.82, 127.72, 126.74, 126.69, 126.63, 120.49. Mass spectrum (EI, M^+): 410 *m/z*. M.P.: 163°C.

Synthesis of 4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane **S7**

Compound **S6** (3.00 g, 7.3 mmol), bis(pinacolato)diboron (2.24 g, 8.8 mmol), potassium acetate (2.87 g, 29.2 mmol) and $Pd(dppf)Cl_2$ (266 mg, 0.36 mmol) were dissolved in 30 mL anhydrous 1,4-dioxane. The reaction mixture was stirred under reflux for 12 hours. After filtrating the insoluble solid and concentrating, the residue was extracted with DCM and brine, dried with anhydrous $MgSO_4$ and removed the solvent. The crude solid was purified by column chromatography (ether: hexane, 1:9 (v/v)) to give a white solid with a yield of 63% (2.05g).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (d (AA'BB'), 2H, J = 8.1 Hz), 7.12-7.06 (m, 9H), 7.06-6.98 (m, 8H), 1.32(s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.80, 143.73, 143.63, 143.55, 141.42, 140.88, 134.13, 131.38, 131.35, 131.34, 130.73, 127.76, 127.69, 126.59, 126.49, 126.48, 83.71, 24.94. Mass spectrum (ESI, M^+): 459 *m/z*. M.P.: 158°C.

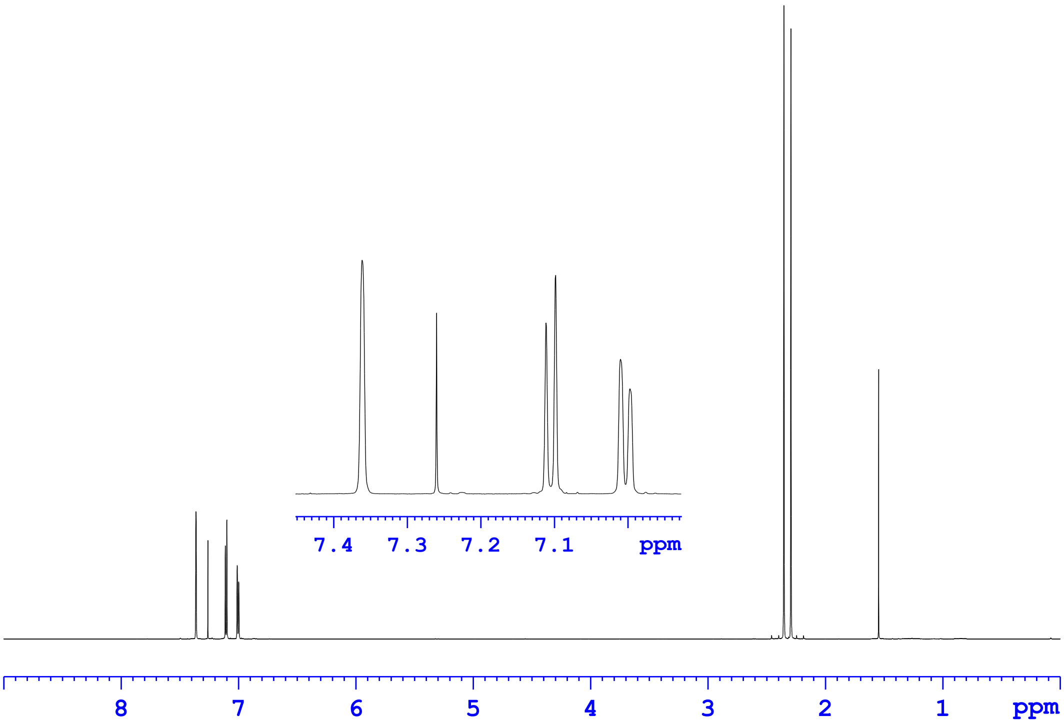


Figure S1. ^{1}H NMR spectrum of **S1** in $CDCl_3$.

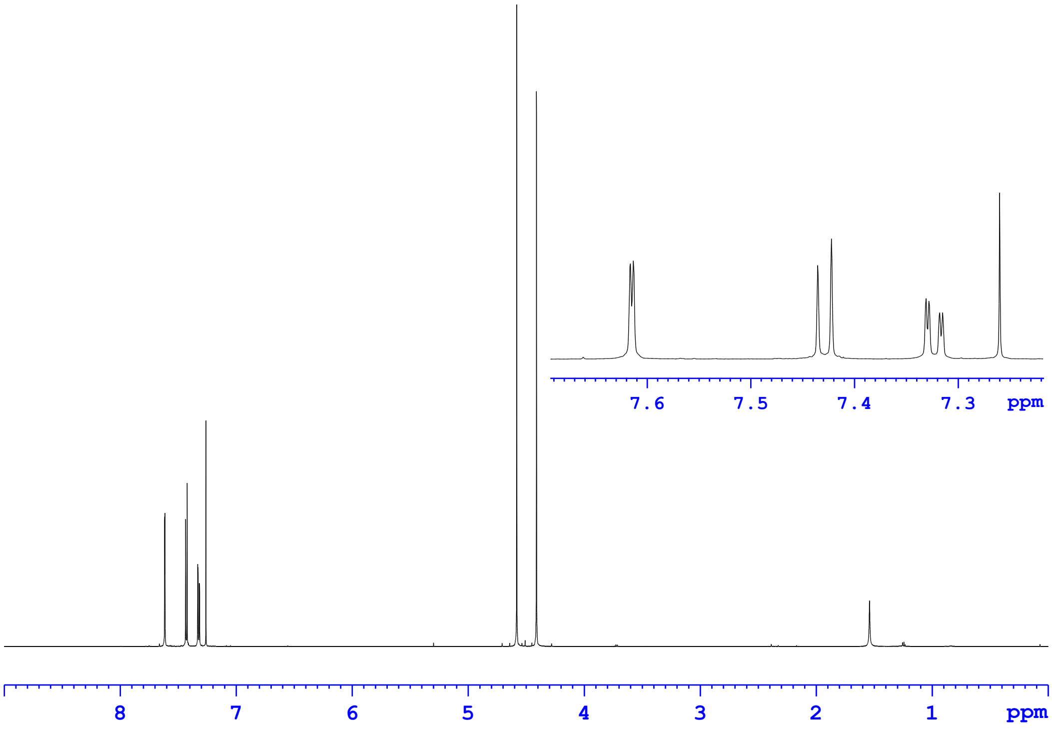


Figure S2. ^{1}H NMR spectrum of **S2** in $CDCl_3$.

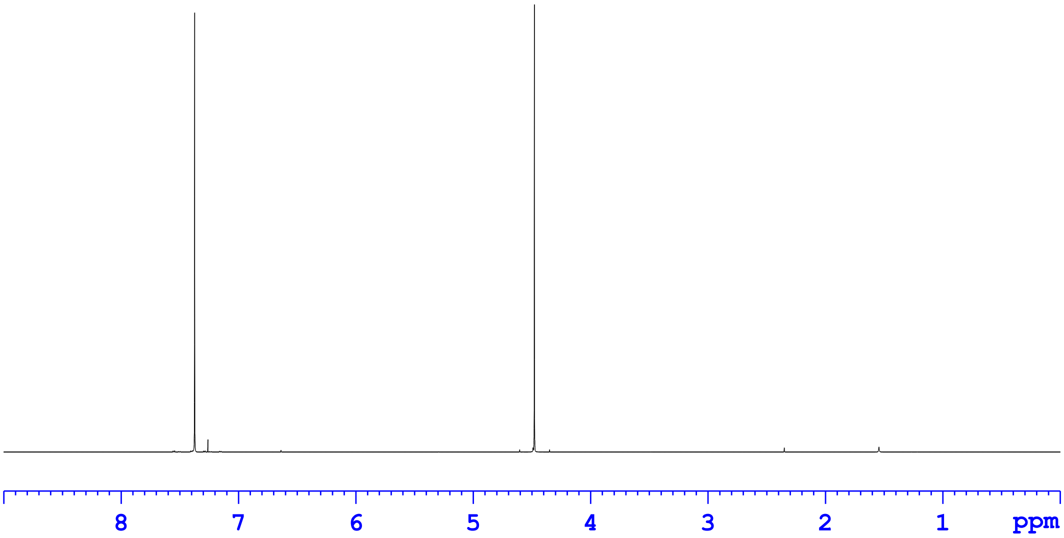


Figure S3. ^{1}H NMR spectrum of **S3** in $CDCl_3$.

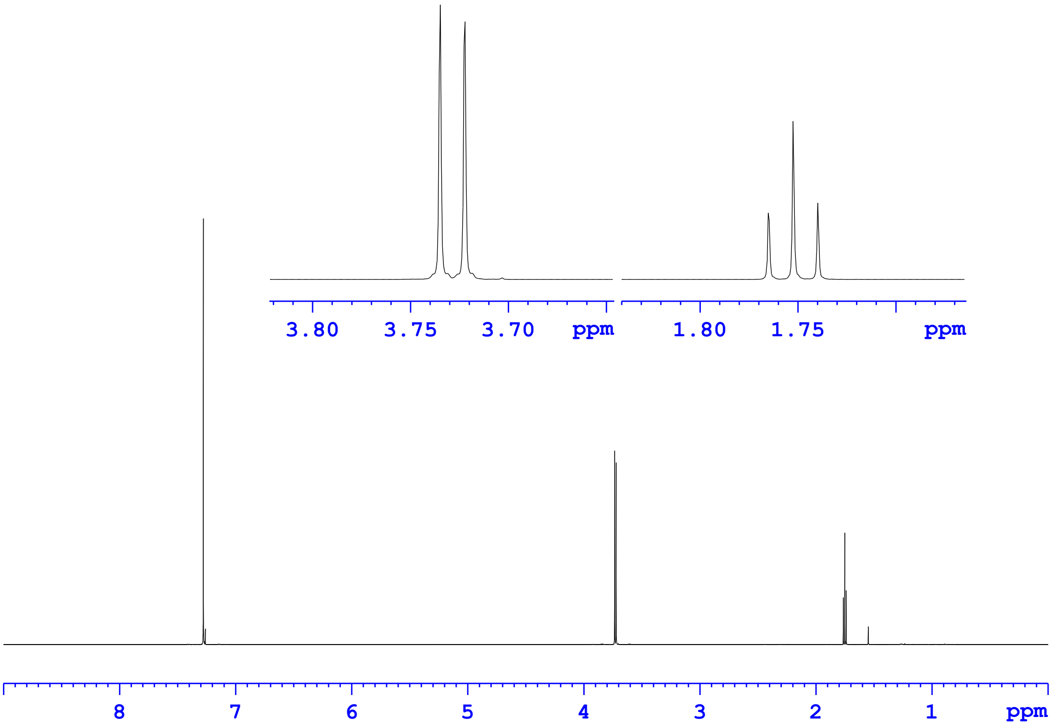


Figure S4. ^{1}H NMR spectrum of **S4** in $CDCl_3$.

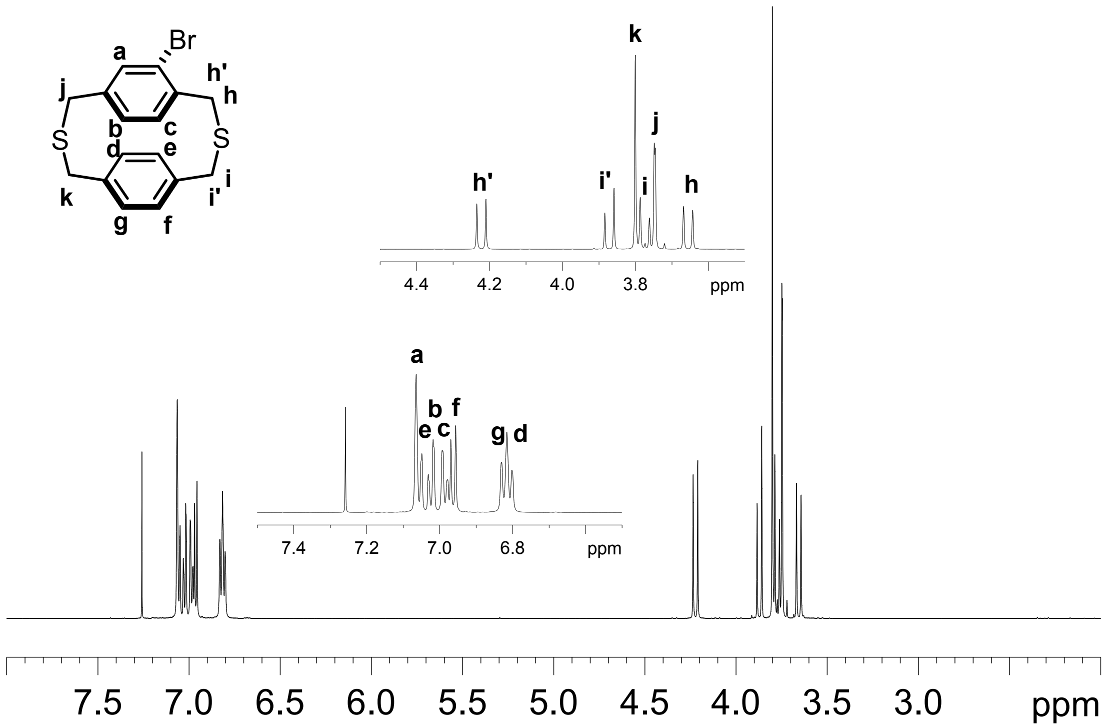


Figure S5. ^{1}H NMR spectrum of **1** in $CDCl_3$.

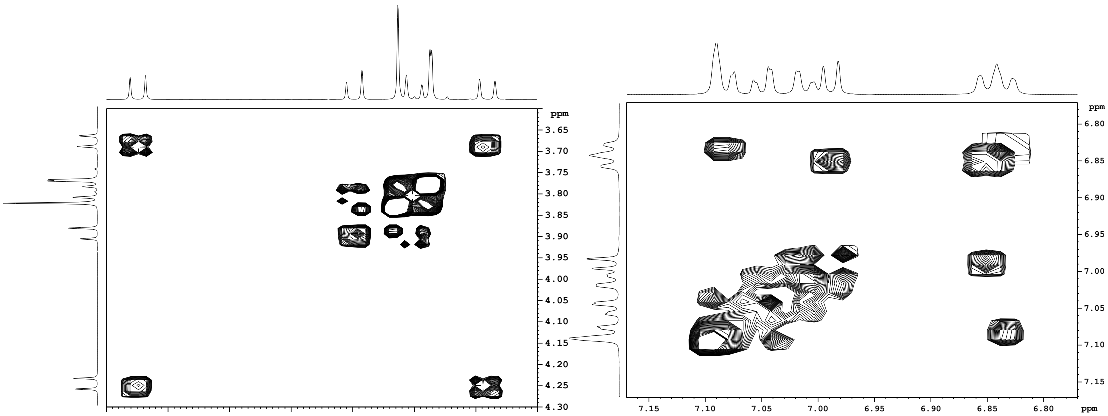


Figure S6. ^{1}H-^{1}H COSY NMR spectrum of **1**.

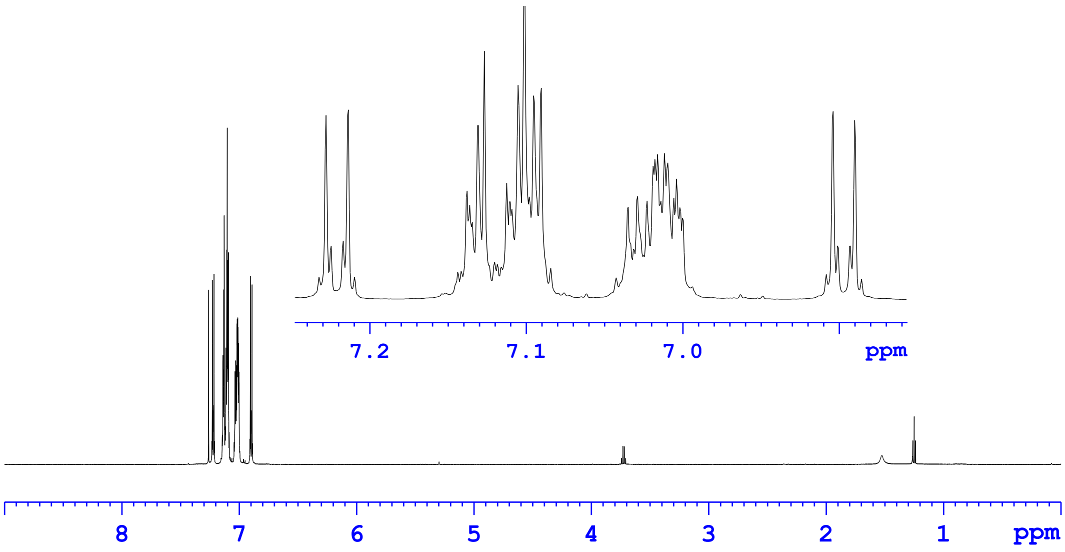


Figure S7. ^{1}H NMR spectrum of **S6** in $CDCl_3$.

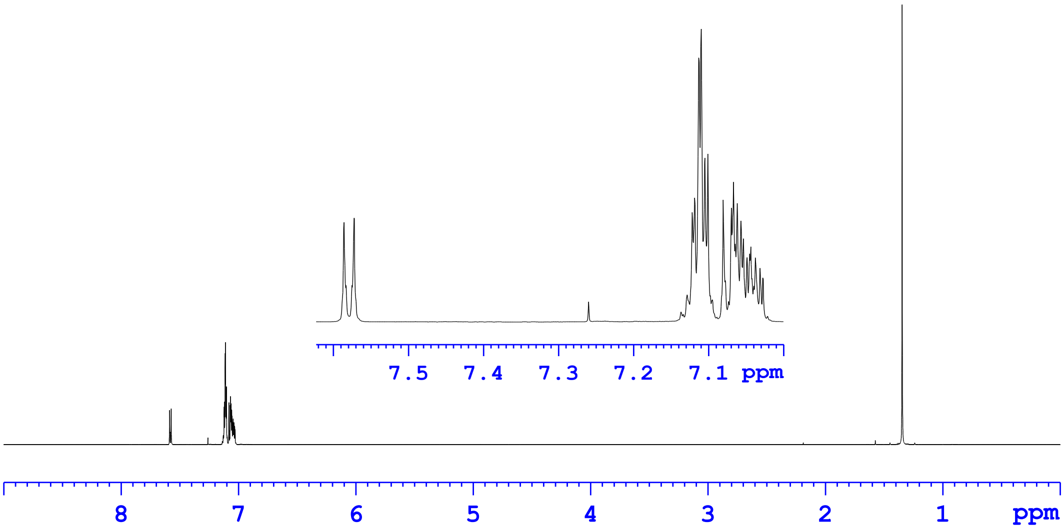


Figure S8. ^{1}H NMR spectrum of **S7** in $CDCl_3$.

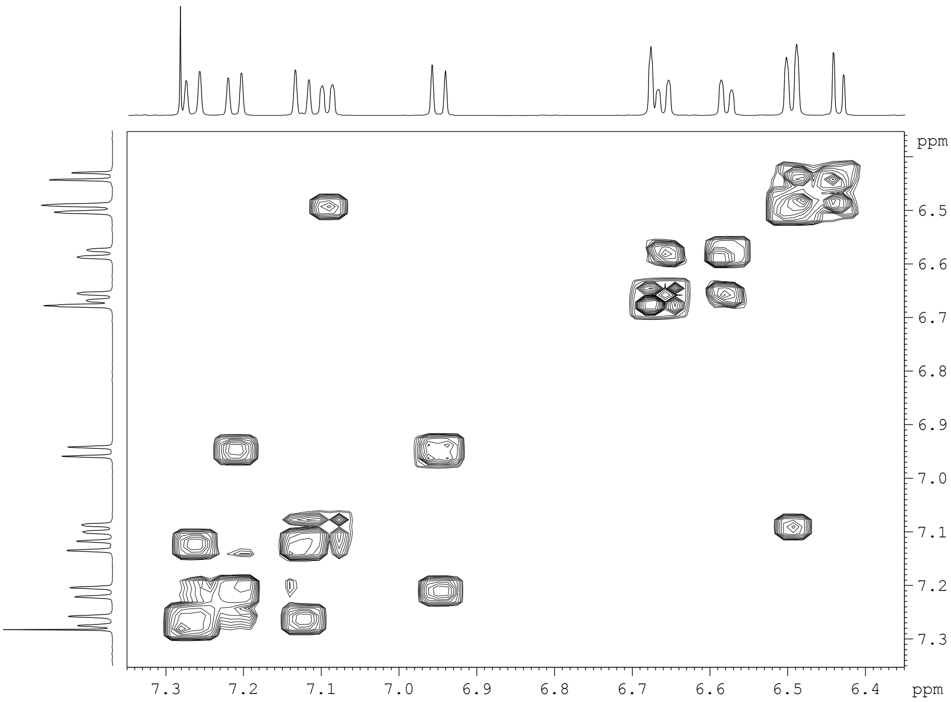


Figure S9. ^{1}H-^{1}H COSY NMR spectrum of **Br-PCPDE**.

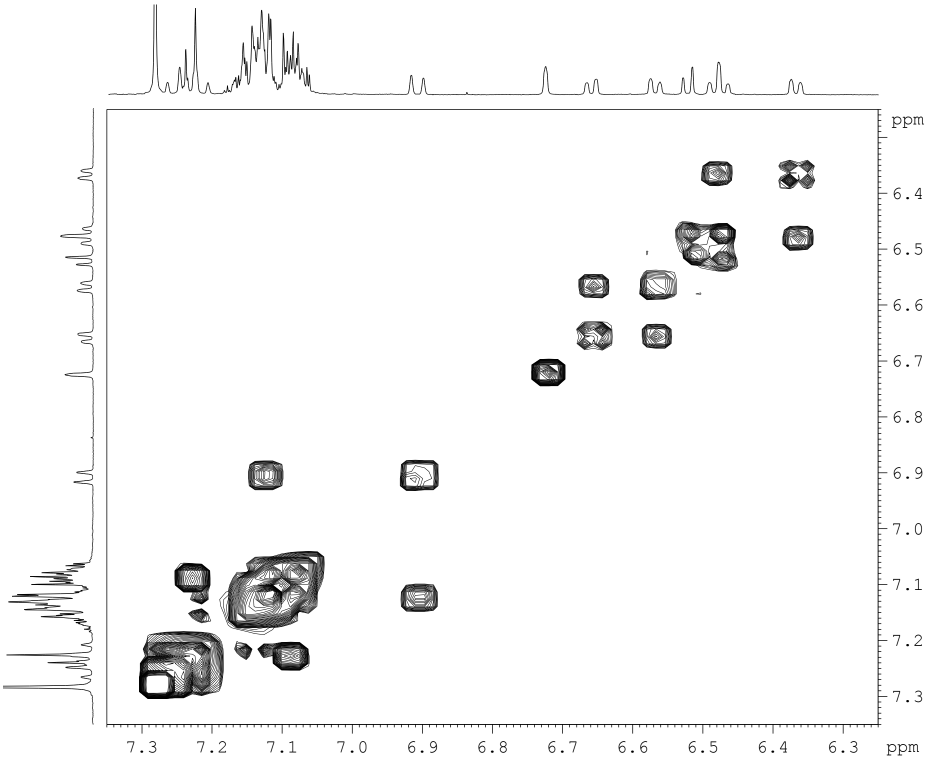


Figure S10. ^{1}H-^{1}H COSY NMR spectrum of **TPE-PCPDE**.

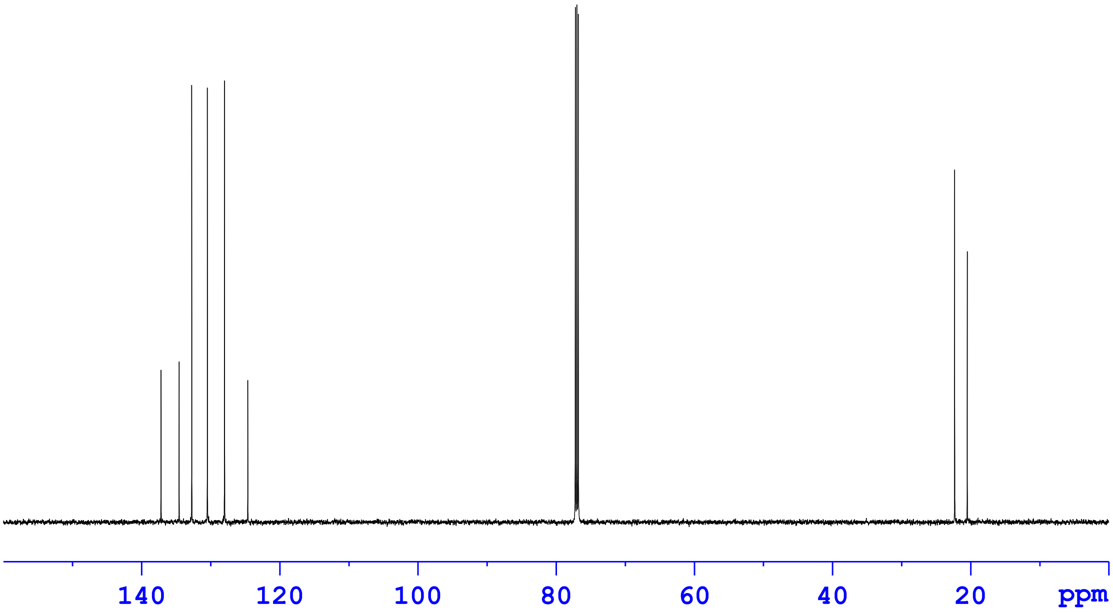


Figure S11. ^{13}C NMR spectrum of **S1** in $CDCl_3$.

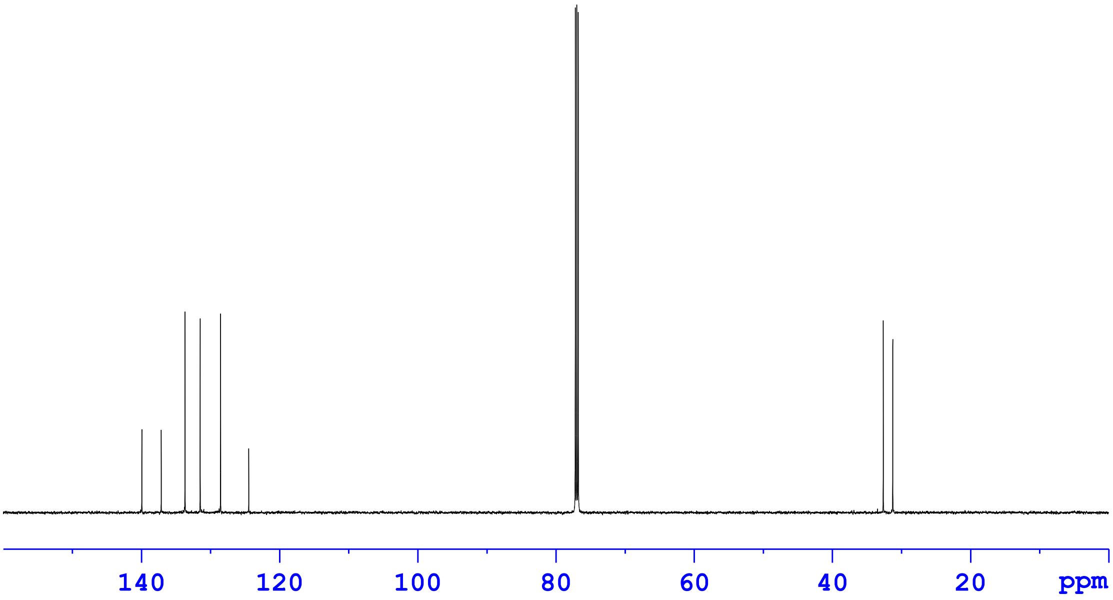


Figure S12. ^{13}C NMR spectrum of **S2** in $CDCl_3$.

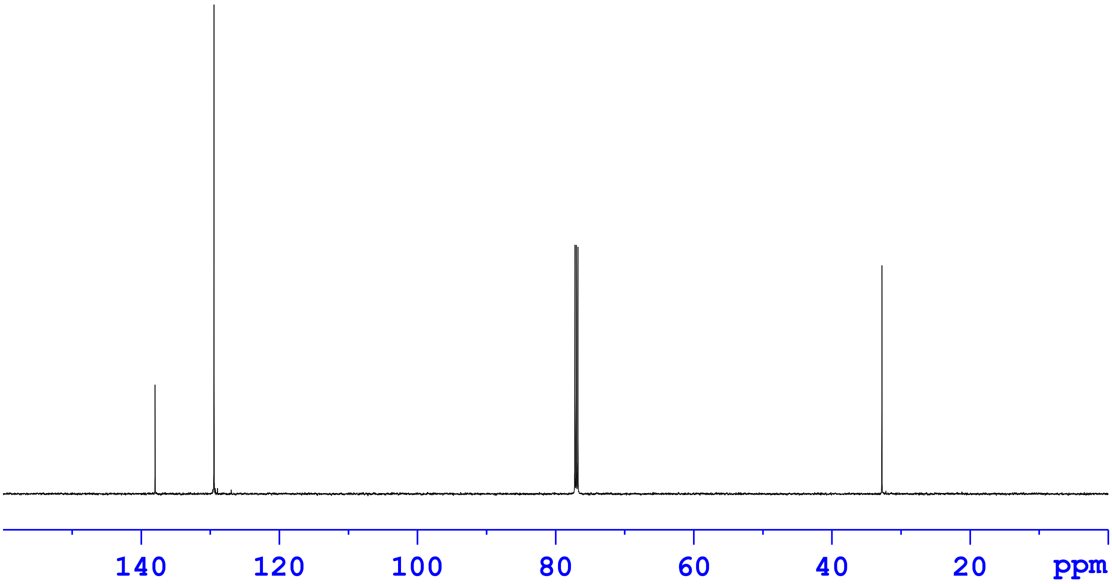


Figure S13. ^{13}C NMR spectrum of **S3** in $CDCl_3$.

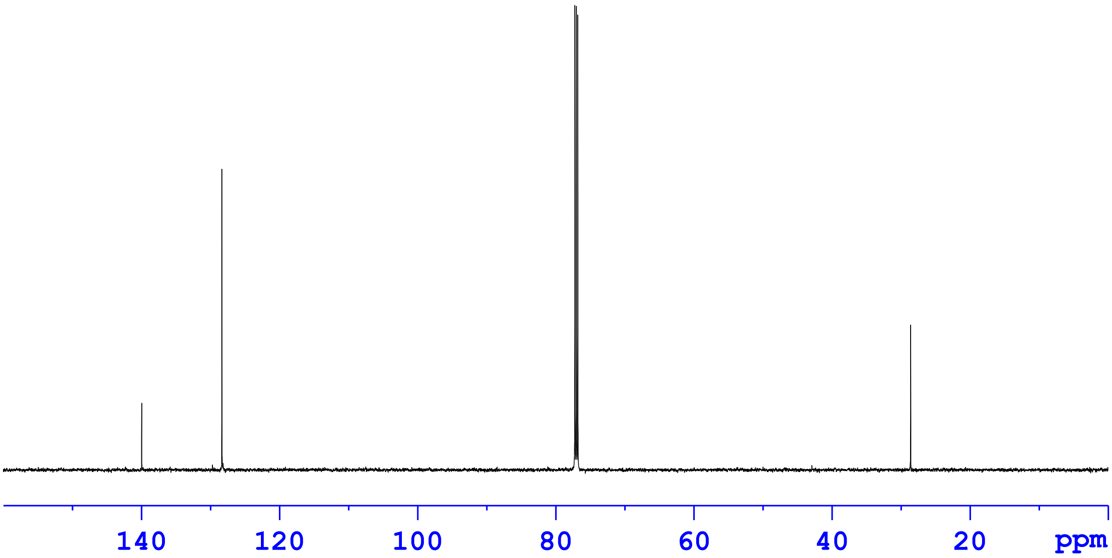


Figure S14. ^{13}C NMR spectrum of **S4** in $CDCl_3$.

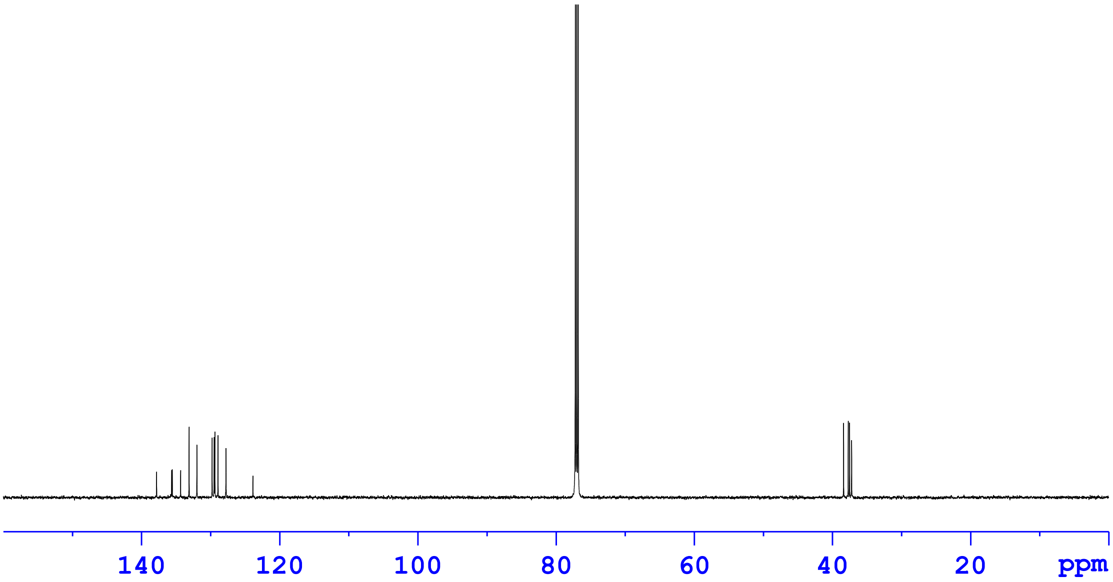


Figure S15. ^{13}C NMR spectrum of **1** in $CDCl_3$.

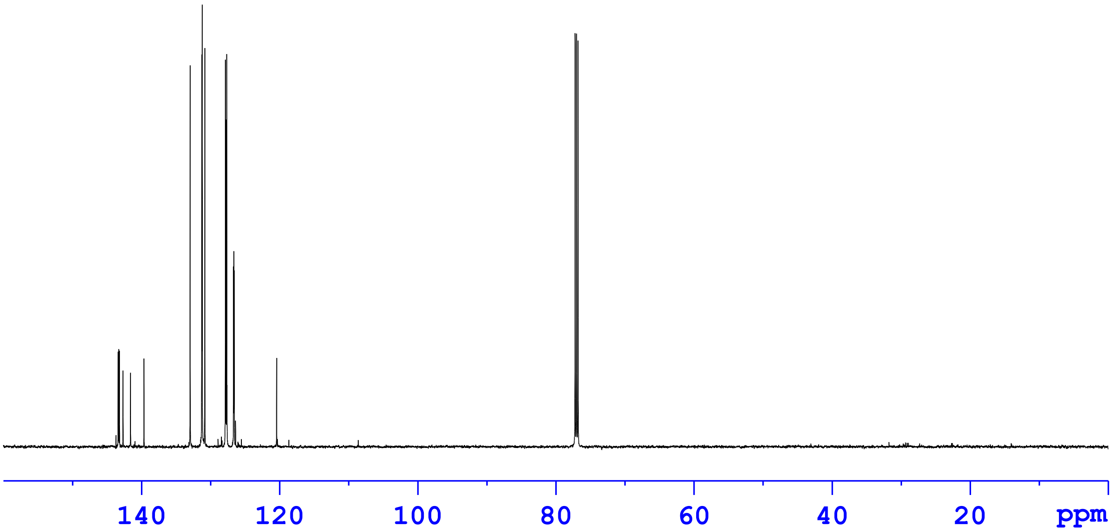


Figure S16. ^{13}C NMR spectrum of **S6** in $CDCl_3$.

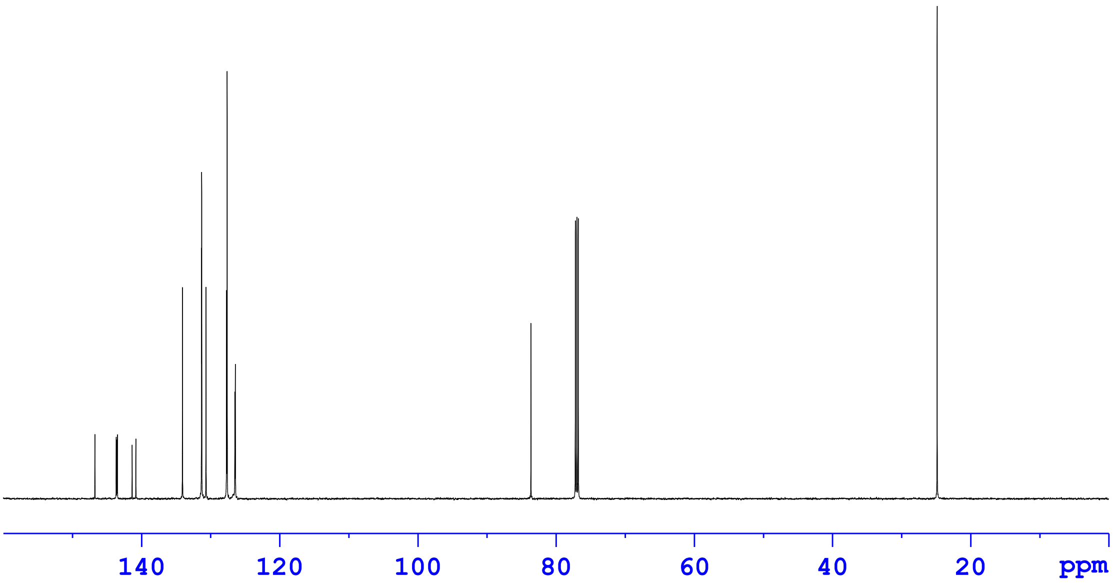


Figure S17. ^{13}C NMR spectrum of **S7** in $CDCl_3$.

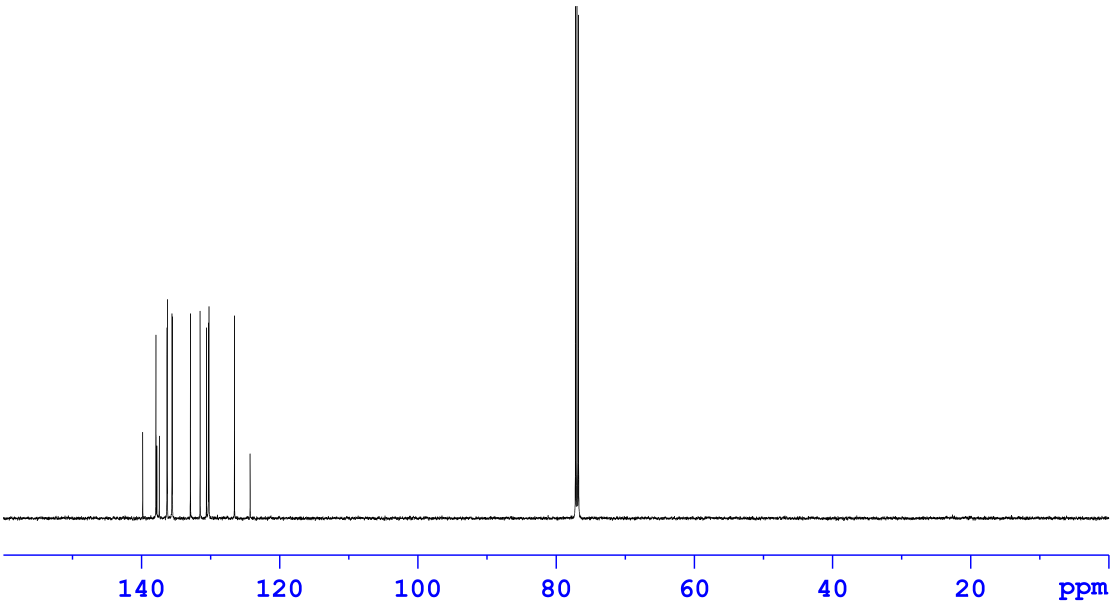


Figure S18. ^{13}C NMR spectrum of **Br-PCPDE** in $CDCl_3$.

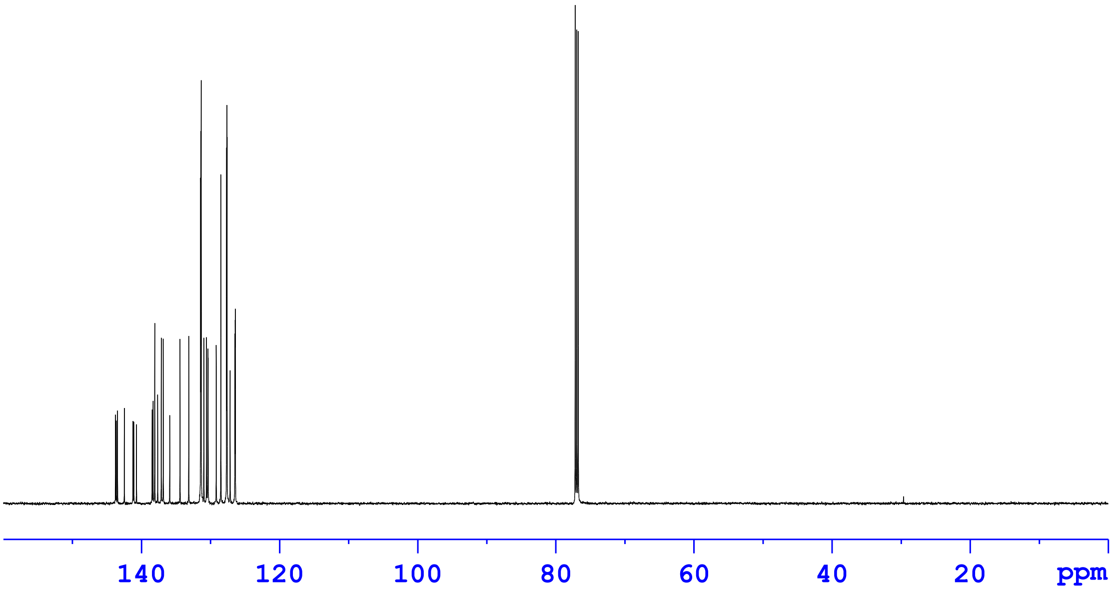
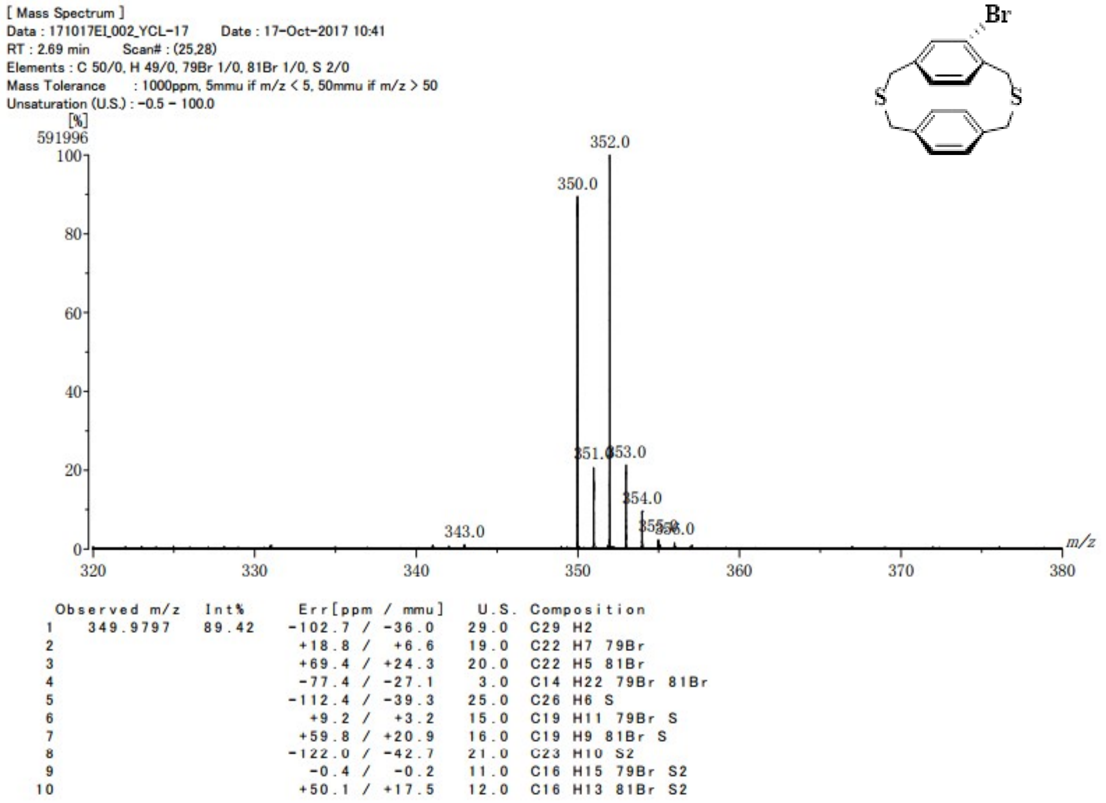


Figure S19. ^{13}C NMR spectrum of **TPE-PCPDE** in $CDCl_3$.



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[ Mass Spectrum ]
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RT : 2.69 min        Scan# : (25,28)
Elements : C 50/0, H 49/0, 79Br 1/0, 81Br 1/0, S 2/0
Mass Tolerance      : 1000ppm, 5mmu if m/z < 5, 50mmu if m/z > 50
Unsaturation (U.S.) : -0.5 - 100.0
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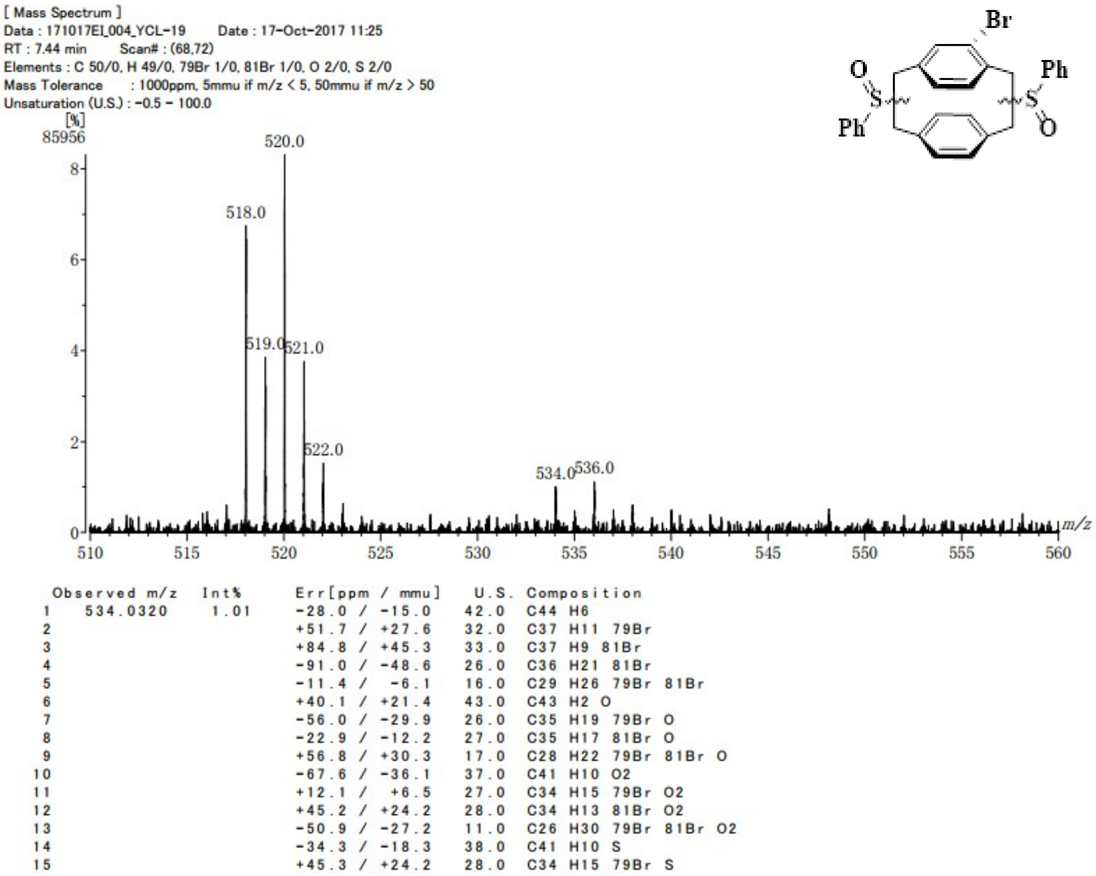
 Observed m/z  Int%     Err[ppm / mmu]   U.S. Composition
 1   349.9797   89.42   -102.7 / -36.0   29.0  C29 H2
 2                       +18.8 /  +6.6   19.0  C22 H7 79Br
 3                       +69.4 / +24.3   20.0  C22 H5 81Br
 4                       -77.4 / -27.1    3.0  C14 H22 79Br 81Br
 5                      -112.4 / -39.3   25.0  C26 H6 S
 6                        +9.2 /  +3.2   15.0  C19 H11 79Br S
 7                       +59.8 / +20.9   16.0  C19 H9 81Br S
 8                      -122.0 / -42.7   21.0  C23 H10 S2
 9                        -0.4 /  -0.2   11.0  C16 H15 79Br S2
10                       +50.1 / +17.5   12.0  C16 H13 81Br S2
```

Figure S20. HREI mass spectrum of compound **1**.



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[ Mass Spectrum ]
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RT : 7.44 min       Scan# : (68,72)
Elements : C 50/0, H 49/0, 79Br 1/0, 81Br 1/0, O 2/0, S 2/0
Mass Tolerance       : 1000ppm, 5mmu if m/z < 5, 50mmu if m/z > 50
Unsaturation (U.S.) : -0.5 - 100.0
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```
 Observed m/z   Int%      Err[ppm / mmu]    U.S.  Composition
 1   534.0320    1.01     -28.0 / -15.0     42.0  C44 H6
 2                        +51.7 / +27.6     32.0  C37 H11 79Br
 3                        +84.8 / +45.3     33.0  C37 H9 81Br
 4                        -91.0 / -48.6     26.0  C36 H21 81Br
 5                        -11.4 /  -6.1     16.0  C29 H26 79Br 81Br
 6                        +40.1 / +21.4     43.0  C43 H2 O
 7                        -56.0 / -29.9     26.0  C35 H19 79Br O
 8                        -22.9 / -12.2     27.0  C35 H17 81Br O
 9                        +56.8 / +30.3     17.0  C28 H22 79Br 81Br O
10                        -67.6 / -36.1     37.0  C41 H10 O2
11                        +12.1 /  +6.5     27.0  C34 H15 79Br O2
12                        +45.2 / +24.2     28.0  C34 H13 81Br O2
13                        -50.9 / -27.2     11.0  C26 H30 79Br 81Br O2
14                        -34.3 / -18.3     38.0  C41 H10 S
15                        +45.3 / +24.2     28.0  C34 H15 79Br S
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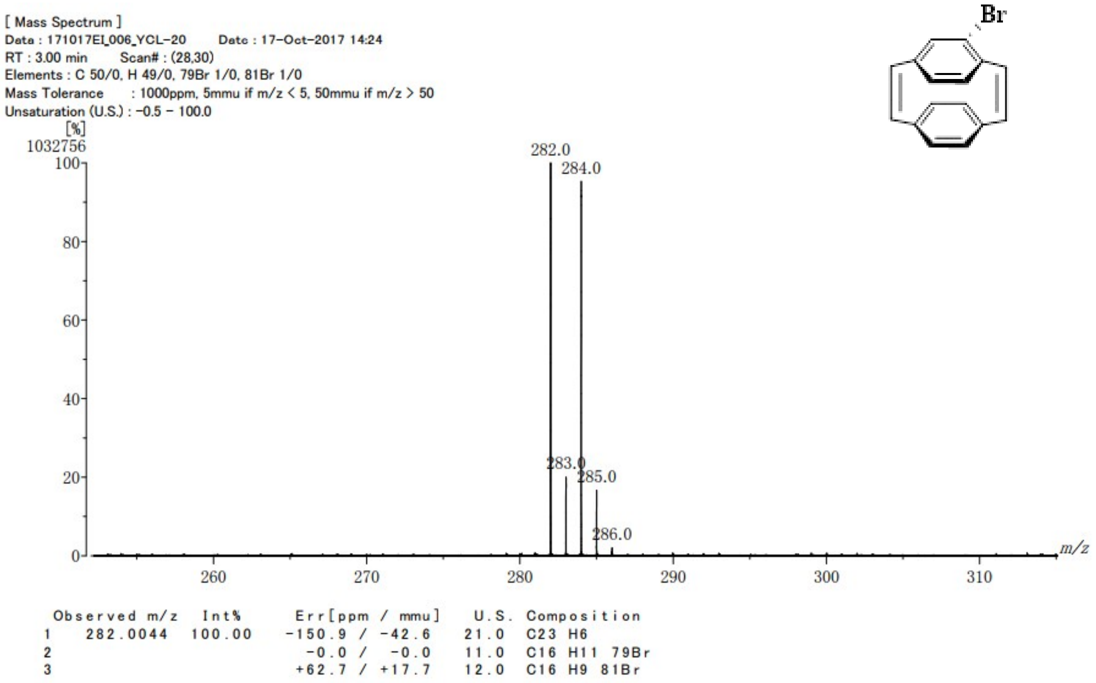
Figure S21. HREI mass spectrum of compound **2**.



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RT : 3.00 min       Scan# : (28,30)
Elements : C 50/0, H 49/0, 79Br 1/0, 81Br 1/0
Mass Tolerance       : 1000ppm, 5mmu if m/z < 5, 50mmu if m/z > 50
Unsaturation (U.S.) : -0.5 - 100.0
```

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 Observed m/z   Int%      Err[ppm / mmu]    U.S.  Composition
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 2                         -0.0 /  -0.0     11.0  C16 H11 79Br
 3                        +62.7 / +17.7     12.0  C16 H9 81Br
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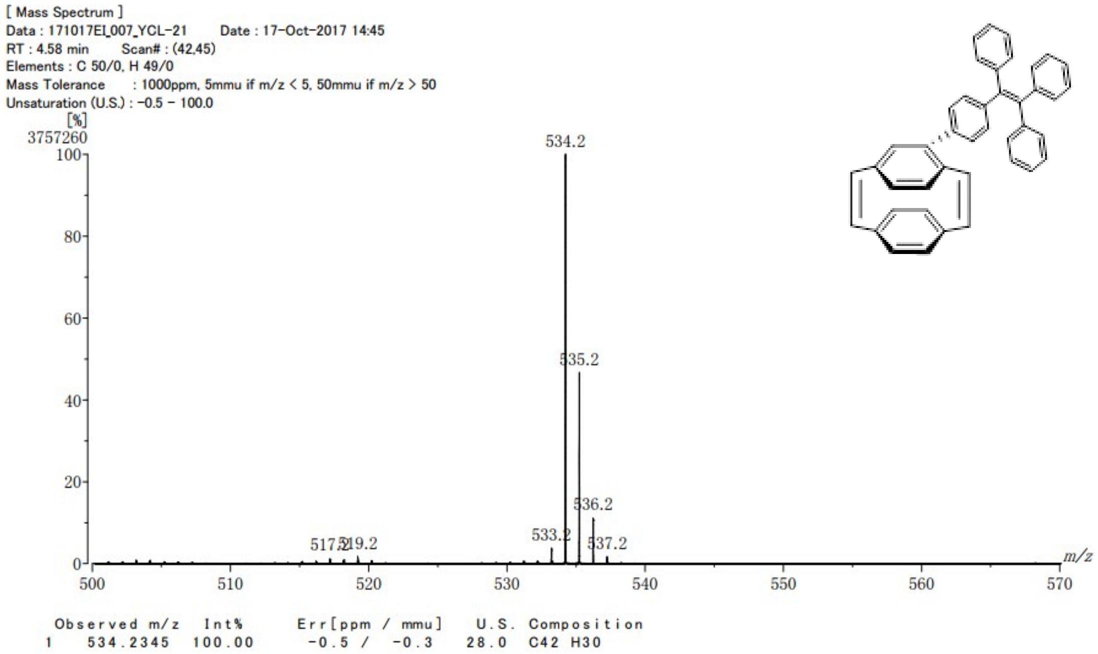
Figure S22. HREI mass spectrum of **Br-PCPDE**.



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[ Mass Spectrum ]
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RT : 4.58 min       Scan# : (42,45)
Elements : C 50/0, H 49/0
Mass Tolerance      : 1000ppm, 5mmu if m/z < 5, 50mmu if m/z > 50
Unsaturation (U.S.) : -0.5 - 100.0
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```
  Observed m/z   Int%      Err[ppm / mmu]    U.S.  Composition
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Figure S23. HREI mass spectrum of **TPE-PCPDE**.

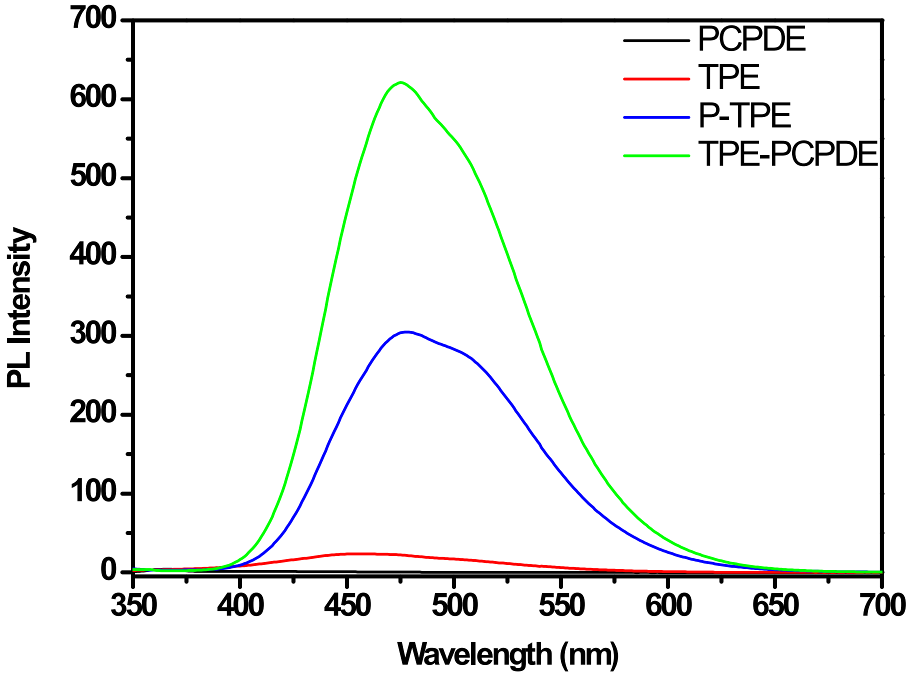

Figure S24. Photoluminescence spectra of **PCPDE**, **TPE**, **P-TPE** and **TPE-PCPDE** in 90% water contents.

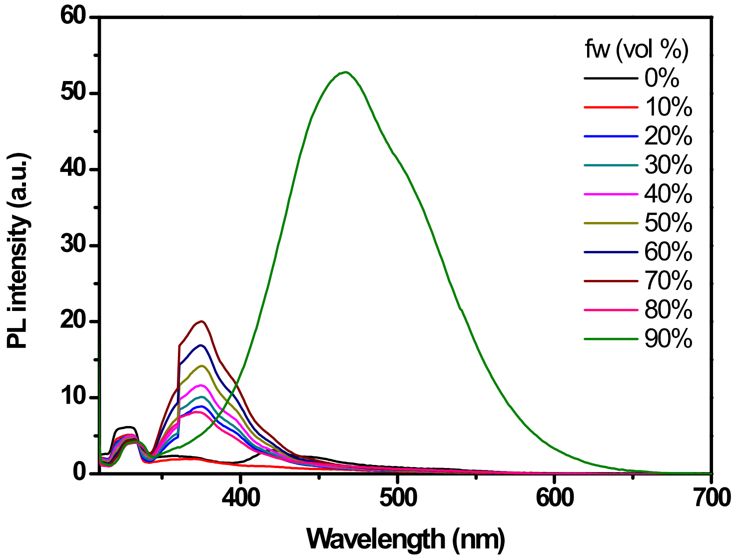

Figure S25. Photoluminescence spectra of **TPE** in THF/water mixtures with different water fractions (initial concentration: 2×10^{-6} M).

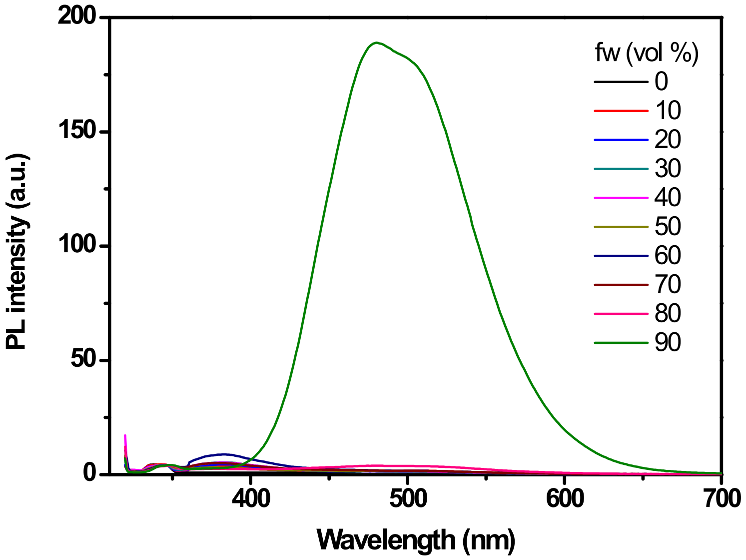

Figure S26. Photoluminescence spectra of **P-TPE** in THF/water mixtures with different water fractions (initial concentration: 2×10^{-6} M).

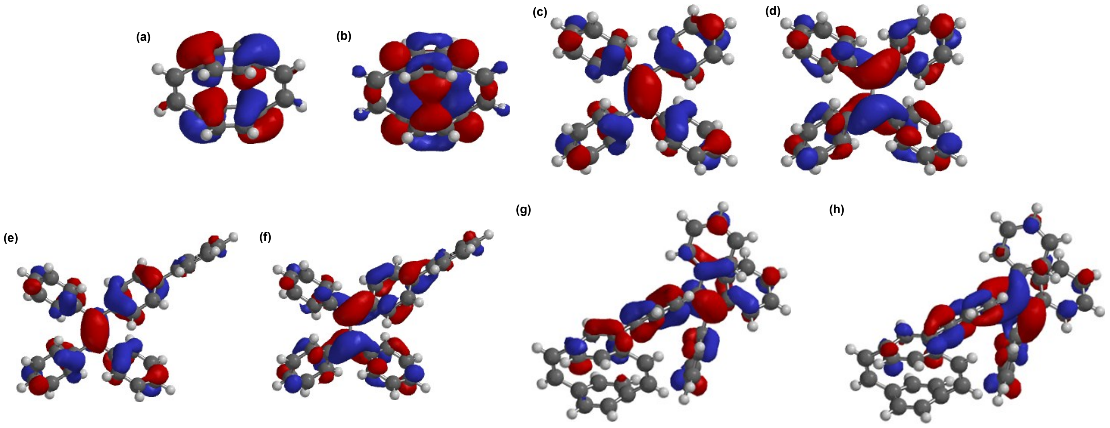

Figure S27. The HOMO structures of (a) **PCPDE**, (c)**TPE**, (e) **P-TPE** and (g) **TPE-PCPDE** and LUMO structures of (b) **PCPDE**, (d)**TPE**, (f) **P-TPE** and (h) **TPE-PCPDE** calculated by density function theory (B3LYP functional, 6-31G* basis set).

Table S1. The HOMO and LUMO levels and bandgaps of **PCPDE**, **TPE**, **P-TPE** and **TPE-PCPDE** calculated by density function theory (B3LYP functional, 6-31G* basis set).

Compounds	HOMO level (eV)	LUMO level (eV)	Bandgap (eV)
PCPDE	-5.61	-0.44	5.17
TPE	-5.33	-0.97	4.36
P-TPE	-5.30	-1.05	4.25
TPE-PCPDE	-5.22	-1.07	4.15

Table S1. Crystal data for **TPE-PCPDE**.

Identification code	d19327	
Empirical formula	$C_{42} H_{30}$	
Formula weight	534.66	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.6495(9) Å	α= 90°
	b = 25.376(2) Å	β= 107.672(3)°
	c = 14.0175(13) Å	γ= 90°
Volume	3270.5(5) $Å^3$	
Z	4	
Density (calculated)	1.086 Mg/m^3	
Absorption coefficient	0.061 mm^{-1}	
F(000)	1128	
Crystal size	0.52 x 0.35 x 0.31 mm^3	
Theta range for data collection	2.21 to 25.04°	
Index ranges	-11<=h<=11, -30<=k<=30, -16<=l<=16	
Reflections collected	49860	
Independent reflections	5737 [R(int) = 0.0375]	
Completeness to theta = 25.04°	99.3 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.9812 and 0.9688	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5737 / 0 / 380	
Goodness-of-fit on F^2	1.603	
Final R indices [I>2sigma(I)]	R1 = 0.0978, wR2 = 0.3319	
R indices (all data)	R1 = 0.1113, wR2 = 0.3573	
Extinction coefficient	0.070(16)	
Largest diff. peak and hole	1.343 and -0.428 e.$Å^{-3}$	

Table S2. Crystal data for **Br-PCPDE**.

Identification code	d19302	
Empirical formula	C_{16} H_{11} Br	
Formula weight	283.16	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.8830(16) Å	α= 90°
	b = 11.6713(13) Å	β= 92.738(4)°
	c = 7.3807(8) Å	γ= 90°
Volume	1194.5(2) Å^{3}	
Z	4	
Density (calculated)	1.574 Mg/m^{3}	
Absorption coefficient	3.412 mm^{-1}	
F(000)	568	
Crystal size	0.18 x 0.09 x 0.04 mm^{3}	
Theta range for data collection	2.28 to 25.32°	
Index ranges	-16<=h<=16, -13<=k<=13, -7<=l<=8	
Reflections collected	14005	
Independent reflections	2147 [R(int) = 0.0483]	
Completeness to theta = 25.32°	98.4 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.8756 and 0.5787	
Refinement method	Full-matrix least-squares on F^{2}	
Data / restraints / parameters	2147 / 0 / 154	
Goodness-of-fit on F^{2}	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.1018	
R indices (all data)	R1 = 0.0585, wR2 = 0.1110	
Largest diff. peak and hole	1.443 and -0.454 e.Å^{-3}	